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Synthesis of Hercynite under Air Atmosphere Using $MgAl_2O_4$ Spinel

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In this paper, the effect of MgO and $MgAl_2O_4$ spinel addition on the formation of hercynite phase was studied. For this reason, the stoichiometric mixtures of hematite and calcined alumina with various amounts of MgO were used. Moreover, the mixtures of hematite with various amounts of $MgAl_2O_4$ spinel were prepared. Afterwards, the compositions were fired at 1450 °C under air atmosphere and the phase composition and microstructure of fired samples were studied by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The results showed that MgO addition leads to formation of spinel, which has great effect on the formation of hercynite phase under air atmosphere. Spinel is formed along with hercynite in the composition with addition of MgO. Besides, the hercynite phase can be formed completely in the composition containing 60 wt.% spinel and 40 wt.% hematite.
Keywords: synthesis; hercynite; phase composition; microstructure; spinel.

1. INTRODUCTION

Hercynite ($FeAl_2O_4$) is a mixed oxide normal spinel, where one eighth of the tetrahedral sites are occupied by Fe^{2+} cations and one half of the octahedral sites are occupied by Al^{3+} cations. Sometimes, depending on the synthetic process, the Fe^{3+} cations can also occupy octahedral sites [1, 2]. Crystalline hercynite exhibits a high saturation magnetization (123 emu/g), higher than other magnetic ceramics like magnetite (92 emu/g). Hence, it is interesting to study this material both from the point of view of its structural modification and its potential applications as a semi-hard magnetic ceramic [3]. On the other hand, hercynite provides an excellent combination of physical and chemical properties. The melting point of hercynite is 1780 °C and it has high ductility and flexibility against cracking and spalling [2, 4, 5]. Therefore, hercynite can be used as refractory material. Recently, hercynite has founded applications in produce of refractory bricks, which are used in cement rotary kilns [1, 6]. Due to the practical considerations mentioned above, the synthesis of hercynite has attracted considerable attention. Many researches have been conducted to improve the synthetic procedures in order to reduce the production cost of this material [1 – 3, 7 – 10]. To synthesize hercynite, FeO needs to react with Al_2O_3 in its stable form at the proper temperature (>1400 °C) and partial pressure of oxygen (Po_2); otherwise, the synthesis of hercynite will fail. Recently, Chen et al. [1] synthesized hercynite by a reaction sintering method using industrial alumina, mill scale ($FeO + Fe_2O_3$), and carbon black as starting materials in the presence of nitrogen and solid carbon at high temperatures. In addition, Dutta et al. [2] synthesized nano-crystalline $FeAl_2O_4$ from the heating of iron and aluminum acetylacetonate complexes and studied the magnetic property of the $FeAl_2O_4$ nano-particles [1, 2]. In addition, hercynite was synthesized in an Ar atmosphere by thermal treatment of mechano-chemically activated metal Al and Fe_3O_4 as starting materials. However, Fe, magnesite, or hematite remained in the final product [11]. It was reported that radial combustion experiments were conducted on Fe_2O_3/aluminum thermite thin circular samples. In fact, a stoichiometric ($Fe_2O_3 + 2Al$) and four over aluminized mixtures were tested. The main products were identified as alumina (α-Al_2O_3) and iron (Fe). Meanwhile, a significant amount of hercynite ($FeAl_2O_4$) was detected, decreasing with the aluminum excess in the reactants [8]. Mukhopadhyay et al. [9] developed novel Al_2O_3-$FeAl_2O_4$ nano-composites by precipitation of $FeAl_2O_4$ particles through reduction aging of Al_2O_3-10 wt.% Fe_2O_3 solid solutions in N_2/4%H_2. It has been demonstrated that reduction of the dissolved Fe^{3+} in the Al_2O_3-Fe_2O_3 solid solutions to Fe^{2+} during aging in the reducing atmosphere results in the precipitation of Fe^{2+}-containing second phase particles ($FeAl_2O_4$) due to the low solubility of Fe^{2+} in Al_2O_3 [9, 10]. In all mentioned studies, the hercynite was obtained under partial pressure of oxygen. Therefore, the object of the present work is to investigate the synthesis of hercynite via oxide mixture method under air atmosphere. For this reason, the calcined alumina and hematite were used as raw materials with various amounts of MgO and magnesium aluminate spinel. Then, the prepared samples were fired at 1450 °C under air atmosphere. The diffractometric technique and scanning electron microscope were used for investigations in this study.

2. EXPERIMENTAL

2.1. Raw materials and compositions

Highly pure hematite (Fe_2O_3) and calcined alumina (source of Al_2O_3) were used for the preparation of hercynite ($FeAl_2O_4$). The chemical compositions of used raw materials are given in Table 1. X-ray Fluorescence (XRF) method was used for analysis of major and trace elements in the used raw materials.

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The hematite used in this investigation (derived from Bafgh regions (Iran)) was finely milled mineral supplied by Sepahan Kani Co. The calcined alumina used was a product of Fibrona Co. (HTM 10, India). The caustic magnesite (source of MgO) used in this investigation (derived from Birjand regions (Iran)) was finely milled caustic-calcined magnesite supplied by Arya Kani Sepahan Co. (Iran). The used $MgAl_2O_3$ spinel was a product of White Circle Co. (Spinwhite 78, India). The physical properties of raw materials used are shown in Table 2.

Table 1. Chemical compositions of the raw materials

Oxides (wt.%)	Raw material type			
	Hematite	Calcined alumina	Castic magnesite	Spinel
SiO_2	–	0.02	1.23	0.06
Fe_2O_3	95.60	0.02	0.86	0.10
Al_2O_3	–	99.70	0.75	76.73
TiO_2	1.90	–	0.01	–
Na_2O	–	0.15	0.15	0.15
MnO	2.50	–	–	–
MgO	–	–	96.21	22.78
CaO	–	–	0.32	0.18
L.O.I	–	0.11	0.47	–

Specific surface area of the oxide powders was measured by the single-point Brunauer-Emmet-Teller (BET) method using N_2 gas (Model MS-16, Quantachrome Corp, Suoset,NY,USA).

Table 2. The physical properties of raw materials used

Physical property	Raw material type			
	Hematite	Calcined alumina	Magnesite	Spinel
Density (g/cm^3)	5.23	3.92	3.1	3.45
d_{50} (μm)	2.23	4	2.6	2.4
Surface area (m^2/g)	2.1	0.9	1.8	1.9

With respect to the stoichiometric ratio of hercynite as well as the chemical composition of raw materials, detailed in Table 1, the mixture of 33.85 wt.% hematite and 66.15 wt.% calcined alumina was used for the preparation of hercynite. The calcined alumina was substituted by caustic-calcined magnesite in proportions of 3, 6, 9 and 12 wt.%. Moreover, the mixtures of hematite with various amounts of spinel (50, 55 and 60 wt.%) were used.

2.2. Preparation of samples and test methods

The required proportions of the starting materials were ground and homogenized in a laboratory planetary mill for 3 h with distilled water, using corundum balls as the grinding bodies. After being milled, the prepared mixtures were dried and then, were granulated. After that, the granulated powder was formed into briquettes under pressure of 800 kg/cm^2 and then, dried at 110 °C. The firing of samples was carried out at 1450 °C, with a soaking time of 3 h in an electric furnace under air atmosphere [1, 2]. The phase composition and microstructure of fired samples were studied by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The XRD measurements were carried out with a D8ADVANCE, Bruker diffractometer with Cu Kα, Ni-filtered radiation. The proportion of different phases in the fired samples was determined by semi-quantitative XRD analysis (X'Pert High Score software). The fracture surface of fired samples after gold coating was evaluated by scanning electron microscope (SEM, JEOL 5410 LV) equipped with an energy-dispersive spectroscope (EDS).

3. RESULTS AND DISCUSSION

The XRD results of prepared samples containing different amounts of MgO after firing are shown in Fig. 1. Besides, the d-spacing values related to identified phases (Fig. 1) are shown in Table 3.

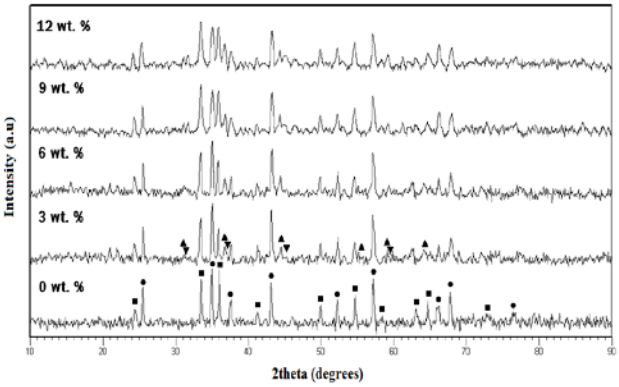

Fig. 1. The XRD results of fired samples containing different amounts of MgO: ■ – hematite; ● – corundum; ▲ – hercynite; ▼ – spinel

Table 3. The d-spacing values related to indentified phases in Fig. 1

Phase	2θ (degree)	d-spacing (Å)
Hematite	33.488	2.67596
Corundum	25.532	3.48885
Hercynite	36.521	2.46038
Spinel	36.842	2.43968

As it can be seen, the hematite (Fe_2O_3) was found in addition to corundum (Al_2O_3) phase as raw materials at composition without MgO; in fact, no hercynite phase was formed in this composition. As stated above, FeO needs to react with Al_2O_3 at high temperature and partial pressure of oxygen (Po_2) to synthesize hercynite [1, 2]. In this study, the stoichiometric ratio of hematite and calcined alumina was fired under air atmosphere (high pressure of oxygen). Therefore, no hercynite was formed under air atmosphere. It can be seen from the results of Fig. 1 that the hercynite phase is formed in the composition with addition of MgO. The broadened diffraction peaks in the XRD results of the samples containing MgO indicate the small grains size and poor crystallinity of the hercynite phase. In addition, the magnesium aluminate spinel phase (MgA_2O_4) is formed with addition of MgO. With respect to results of Fig. 1, the peaks of spinel and hercynite phases are very similar. Besides, according to results of Table 3, the main peaks of

hercynite and spinel phases are very close together (36.521° and 36.842°, respectively). Therefore, identified peaks at the range of 36.5°–37° confirm the formation of hercynite and spinel in the sample containing MgO. The proportion of the formed phases in the fired samples was determined by semi-quantitative XRD analysis. The results are plotted in Fig. 2 as a function of MgO amount.

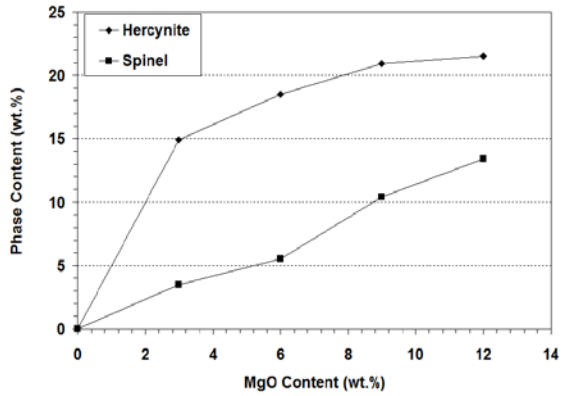

Fig. 2. The effect of MgO addition on the amounts of formed phases content in the fired sample

As it can be seen from the results of Fig. 2, the amount of hercynite in the composition is enhanced with increasing of MgO content in the composition. Furthermore, spinel is formed along with hercynite in the composition with addition of MgO, which their contents are enhanced with increasing of MgO content. Hence, it can be concluded that the content of formed phases in the composition depends on MgO content in the raw materials composition. As stated above, the hercynite phase is formed in the composition with addition of MgO. The observed behavior may be related to the formation of spinel in the composition with addition of MgO, which helps to the formation of hercynite. At first, the formation of spinel phase takes place and then, spinel reacts with hematite grains with the increase of temperature. The reaction between spinel and hematite leads to formation of hercynite. However, reaction between formed spinel and hematite is a solid-state reaction. Hence, the spinel grains must be in contact with hematite grains; otherwise, the formation of hercynite will fail.

As it can be seen from the results of Fig. 2, the spinel is formed along with hercynite in the composition with addition of MgO. Therefore, this detected spinel can be a part of total formed spinel which could not reacte with hematite. Hence, the formed spinel crystals, which are not in contact with hematite grains, do not contribute to the formation of hercynite and can be detected. Therefore, the spinel cannot be fully converted to hercynite and the spinel peaks are appeared in the XRD results with addition of MgO. For the study of spinel role on the formation of hercynite, different amounts of spinel were added to hematite grains instead of magnesite (MgO). Then, the effect of spinel addition on the formation of hercynite was investigated. The XRD results of prepared samples containing different amounts of spinel after firing at 1450 °C are shown in Fig. 3. With respect to these results, the hercynite phase is formed in the composition containing spinel and hematite. The intensity of the diffraction peaks of the hercynite phase gradually enhances by the increase of spinel amount. Hence, the amount of hercynite in the composition is enhanced with increasing of spinel amount.

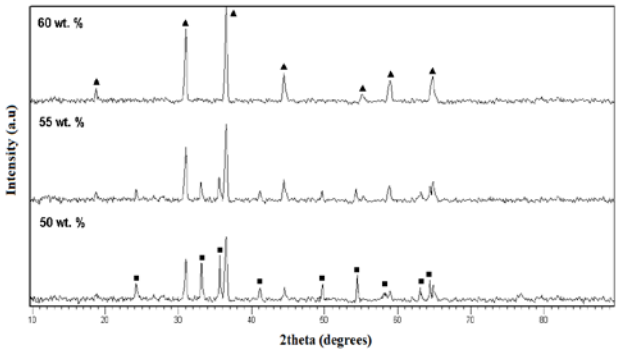

Fig. 3. The XRD results of fired specimens containing different amounts of spinel: ■ – hematite, ▲ – hercynite

It can be seen that the specimen containing 60 wt.% spinel and 40 wt.% hematite mainly contains hercynite phase. In this composition hematite peaks are not observed which indicates the starting materials are completely reacted. Comparison between results of Fig. 1 and Fig. 3 reveals that the use of spinel instead of MgO leads to formation of completely octahedral hercynite in the composition. Besides, diffraction peaks of hercynite in the XRD results of Fig. 3 are sharper than Fig. 1. Sharp diffraction peaks of hercynite in Fig. 3 indicate larger crystallite size and higher crystallinity of the hercynite phase in composition containing spinel and hematite.

In general, spinel is a ternary oxide whose chemical formula is AB_2O_4, where A represent a divalent metal cation that normally occupies a tetrahedral site and B represents trivalent metal cations that normally occupy the octahedral sites of a cubic packed crystal. On the other hand, a complete solid solution exists between spinel ($MgAl_2O_4$) and hercynite ($FeAl_2O_4$) and then, minerals of the $(Mg, Fe^{2+})(Al, Fe^{3+})_2O_4$ system are widespread in most geological environments [2, 12]. Hence, the conversion of Fe^{3+} to Fe^{2+} takes place with increasing of temperature and after that, Fe^{2+} dissolves into spinel structure during firing. Then, the Mg^{2+} in the spinel structure replaces by dissolved Fe^{2+} which, leads to formation of $(Fe/Mg)Al_2O_4$ hercynite. As stated above, the hercynite phase is usually synthesized under inert gas or reduction atmosphere (partial pressure of oxygen) [1–4]. But, the results showed that hercynite can be prepared under air atmosphere by using a mixture oxide method and low cost raw materials. The microstructures of the fired specimens containing 12 wt.% MgO are shown in Figs. 4 and 5.

As it can be seen, the composition containing 12 wt.% MgO contains the crystalline phases, which have hexagonal, cubic and spherical forms. Moreover, the microstructure is porous and there are more pores between particles. According to XRD results of Fig. 1, the present phases in this composition contain hematite, hercynite, corundum and spinel that linked together via sintering process. The results of the EDS analysis showed that the gray hexagonal particles were corundum, whereas the white spherical particles were hematite. Besides, the micrograph of sample containing 12 wt.% MgO (see Fig. 5) shows aggregates with some cluster of cubic shape crystals.

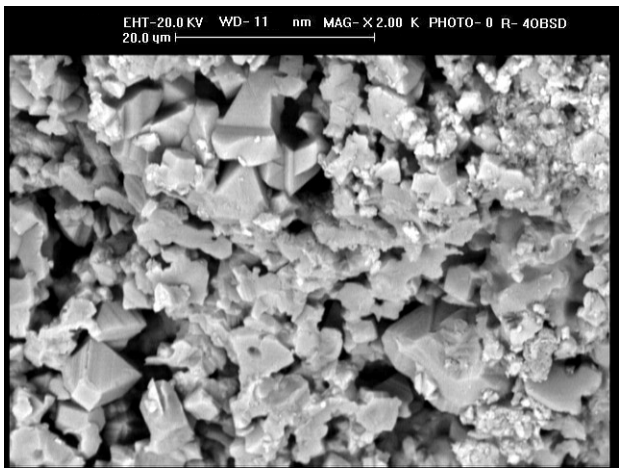

Fig. 4. SEM photomicrograph of fired sample containing 12 wt.% MgO

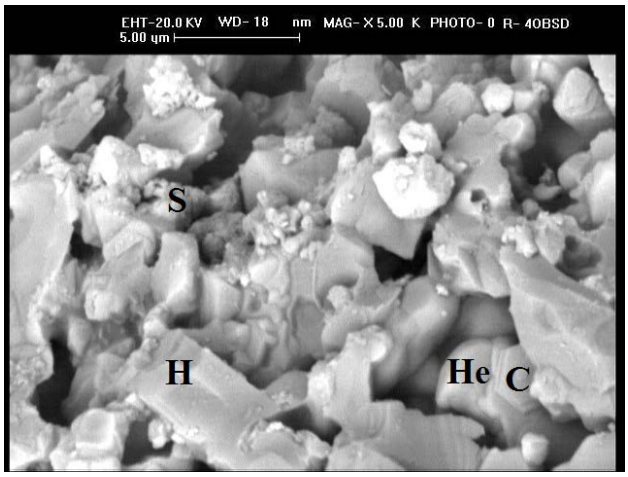

Fig. 5. SEM photomicrograph of fired sample containing 12 wt.% MgO: He – hematite, C – corundum, H – hercynite, S – spinel

The EDS analysis indicates that these cubic crystals are MA spinel phase. Moreover, it was found that many octahedral crystals were formed when the MgO introduces into composition. The EDS analysis these octahedral crystals (point H in Fig. 5) is shown in Fig. 6 and EDAX ZAF Quantification (standardless) oxides is presented in Table 4. According to the EDS analysis (Fig. 6) and EDAX ZAF Quantification (standardless) oxides (Table 4), these octahedral grains were $Fe(Mg)O.Al_2O_3$, which could be considered as the solid solution based on hercynite.

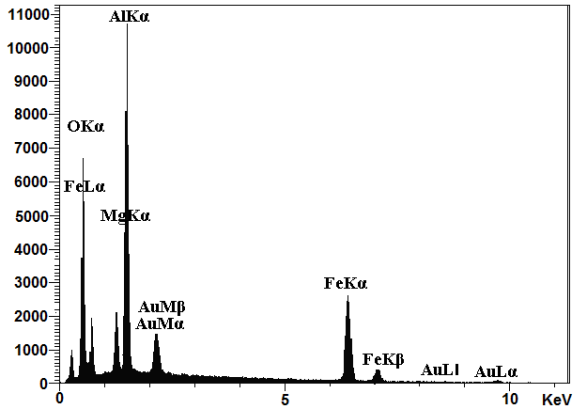

Fig. 6. The SEM/EDX analysis of octahedral grains in Fig. 5

Table 4. EDAX ZAF Quantification (standardless) oxides in Fig. 6

Element	Intensity	wt. %	At. %	ZAF
O	600.7	37.19	61.88	0.5397
Mg	178.8	3.89	4.26	0.5479
Al	1041.4	19.18	18.92	0.6359
Fe	430.5	27.98	13.34	0.8935
Au	5.5	11.76	1.59	0.6039
Total		100.00	100.00	

The microstructural evaluation of all samples showed that further addition of MgO leads to the formation of higher octahedral hercynite in the composition. Meanwhile, the grain size of the formed hercynite increases by the addition of further MgO. The grain size distribution of the formed hercynite in composition containing 12 wt.% MgO is in the range of about 3 µm – 5 µm.

Figs. 7 and 8 demonstrate the microstructures of fired samples containing 60 wt.% spinel and 40 wt.% hematite. With microstructural evaluation, one can see that the well-crystallized grains of hercynite are formed and connected with each other, indicating that the hercynite synthesised using spinel is of high purity.

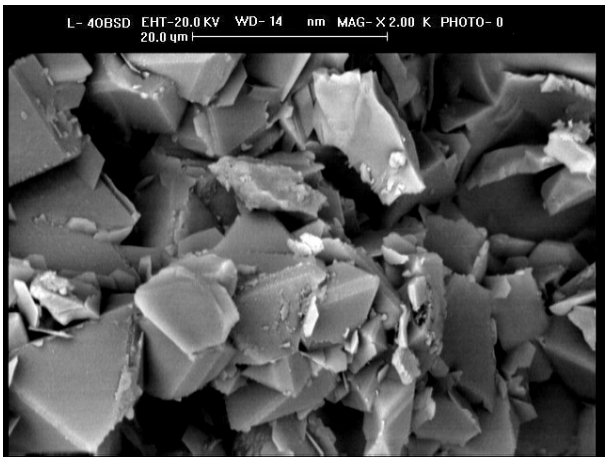

Fig. 7. SEM photomicrograph of fired sample containing 60 wt.% spinel

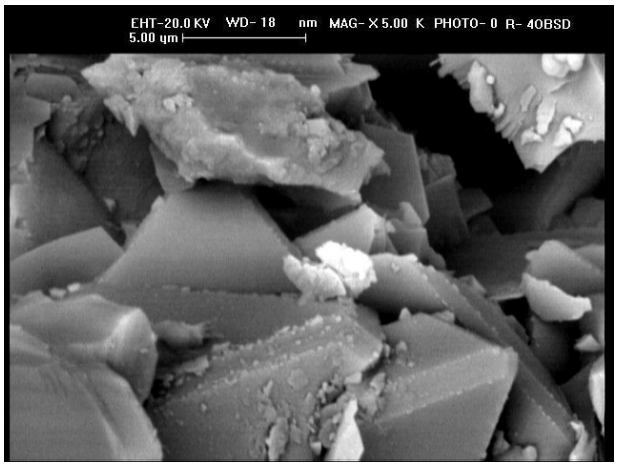

Fig. 8. SEM photomicrograph of fired sample containing 60 wt.% spinel

The microstructural evaluation of this sample shows a heterogeneous structure which, the octahedral grains of hercynite with different sizes are formed. This microstruc-

ture does not show a dense structure and there are more pores between particles. By making a comparison between microstructures of composition containing 12 wt.% MgO (Fig. 4) and composition containing 60 wt.% spinel (Fig. 7), one can see that the addition of spinel instead of MgO causes a drastic change in particles size and morphology of hercynite. Hence, the exaggerated grain growth is observed, and the completely solid-state reaction between spinel and hematite is occurred in fired samples at 1450 °C.

The microstructural evaluation of all samples showed that the grain size of the formed hercynite increases by the addition of further spinel. The grain size distribution of the formed hercynite in composition containing 60 wt.% spinel and 40 wt.% hematite is in the range of about 10 μm – 12 μm. It can be seen from SEM photomicrographs of Figs. 4 and 7 that higher porosity in the microstructure of sample containing spinel is produced. It can be related to the exaggerated grain growth of hercynite in composition containing spinel.

4. CONCLUSIONS

Hercynite was synthesized at 1450 °C under air atmosphere by a reaction sintering method using starting materials of calcined alumina, hematite and MgO addition. The results showed that the hercynite formation takes place in presence of MgO. In addition, MgO addition influences the amount of hercynite phase so that the hercynite amount is enhanced with increasing of MgO amount. MgO addition leads to formation of spinel, which has great effect on the formation of hercynite phase under air atmosphere. Spinel is formed along with hercynite in the composition containing MgO. The conversion of Fe^{3+} to Fe^{2+} takes place with increasing of temperature and after that, Fe^{2+} dissolves into spinel structure during firing. The Mg^{2+} in the spinel structure replaces by dissolved Fe^{2+} which, leads to formation of $(Fe/Mg)Al_2O_4$ hercynite. Besides, the hercynite phase is formed completely in the composition containing spinel and hematite. This method is presented an interesting alternative for the preparation of hercynite, which can permit to obtain hercynite in air atmosphere.

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